

Chemical and mechanical performance of flexible magnetic tape containing chromium dioxide

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The development of a magnetic-recording tape using chromium dioxide suitable for use with the tape drive of the IBM 3480 Magnetic Tape Subsystem was found to require careful optimization of the chemical and mechanical properties of the coating. This paper discusses the role of chromium dioxide in the oxidative and hydrolytic degradation of the polyester-polyurethane binders used in most flexible tape coatings, and the subsequent necessity for careful binder selection to eliminate (for all practical purposes) these degradative effects. In addition to the chemical behavior, the paper discusses the role of the interaction of the chromium dioxide with the binder necessary to obtain mechanical performance suitable for the 3480 tape drive. A high modulus and a relatively high glass-transition temperature were found to be required to avoid changes in the frictional properties of the tape. The incorporation of a rough-textured back coat was found to control the change in the surface topography of the recording surface near the spool hub which arises as a result of compressive forces.

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Introduction

To continue to increase the density of data storage and data rate, elements that are driving digital-recording technology [1], there is a migration to higher-coercivity particles to provide tapes with improved performance. Chromium dioxide particles, which possess the appropriate magnetic properties, presented an opportunity for a major improvement in tape performance, provided that a formulation could be developed that would reduce the chemical instability of the particles [2, 3]. This paper discusses the effort involved in the formulation of a flexible tape containing chromium dioxide and the impact of chromium dioxide on the mechanical performance of these tapes.

Study of the chemical performance involved examination of the particle-binder interactions and the susceptibility of chromium-dioxide tape to chemical and physical changes upon exposure to humid or thermal aging. The tribological properties and the maintenance of stable surface topography required considerable study and optimization of the mechanical properties of the magnetic-coating layer. Selection of thermomechanically stable formulations and the incorporation of a back coat to control the surface topography under the compressive stresses to which the tape surface is exposed were found to result in a durable magnetic tape containing chromium dioxide suitable for the 3480 tape drive.

This paper is divided into two main parts: The first part describes studies of the chemical stability, and the second, work on the mechanical stability of chromium-dioxide-based tape.

Chemical stability

Although the chemistry of chromium oxides has received considerable study, the investigation of chromium-dioxide chemistry has been rather limited, with most of the effort having occurred in the last 20 years [3, 4] despite its characterization in 1935 [5]. It is noted that chromium dioxide is metastable in air and exists in solution only as reactive intermediates in the course of oxidation-reduction reactions [4]. Early patents relevant to the use of chromium dioxide in the manufacture of magnetic tape claimed that a surface treatment or stabilization of the chromium-dioxide particles is required to stabilize the magnetic properties of the finished medium [5, 6-8]. Little reference has been made, however, to the impact of this instability on the integrity of the coating and the chemistry of the binder resin.

The binders commonly used in the fabrication of flexible magnetic tape are elastomeric polyurethanes, polyvinyls, and combinations of these two major families of polymers. Other polymeric additives are often used to achieve the desired hardness, flexibility, toughness, and adhesion. Additional components such as lubricants, dispersants, and curative agents are also commonly added to the coating formulation. More details of the state of the art in magnetic-tape formulations are available in several recent reviews [2, 3, 9].

Chemical analysis of tape samples containing chromium dioxide in various binder formulations, which had been exposed to thermal and humid aging, indicated changes in both the chemical functionality and the molecular weight of the polymer. An understanding of the mechanism of the interaction of the chromium dioxide with the binder and of the resulting changes in the coating performance was achieved through analysis of solutions and free films of the magnetic inks and from extracts obtained from coated tapes. Both free films and finished tapes were subjected to high temperature and humidity to monitor the effects of these aging environments.

• Experimental

Coatings were made containing acicular chromium dioxide and γ -Fe₂O₃ dispersed into an organic solvent system containing the polymeric binder. Polyurethane binders constructed from 1,4-butanediol (as the hard-segment chain extender) and 4,4-diphenylmethane diisocyanate (MDI) with three soft segments were used. Resin A contains an alcohol-terminated polyester as the soft segment, whereas resin B was constructed from a polyester containing a hindered alcohol. An alcohol-terminated polyether was used as the soft segment in resin C.

All of the coatings contained an equal weight of a fatty acid ester relative to the weight of the polyurethane binder, which serves as a lubricant in the finished tape. This lubricant was found to serve as a reliable internal standard for the tape extracts, being totally extractable by the procedure used. Extraction was carried out using 1 g of

coated tape or 0.1 g of the dried ink in free-film form. The tape sample was extracted by immersion in 150 ml of freshly distilled tetrahydrofuran (THF) for one to two hours at 22-24°C.

After removal of the extract from the insoluble tape residue, the extract was concentrated to 0.5 ml volume by evaporation under reduced pressure. The concentrated extract was then filtered through a 0.45- μ m filter. The evaporation flask was washed with three 0.5-ml rinses of THF and each wash solution filtered through the 0.45- μ m filter. The concentrated extract and the washes were then combined in a 2-ml vial suitable for automatic injection into a high-pressure gel-permeation-chromatography (GPC) apparatus.

A Water's Associates Model 201 high-pressure gel-permeation-chromatography apparatus using a Water's Associates Model 401 differential refractometer as the detector was used to carry out GPC analysis of extracts. A 200- μ l aliquot of the extract was injected using a Water's Associates Model WISP 710B automatic sample injector. Gel-permeation-chromatographic separation of the sample was then carried out through a series of six μ Styragel (trademark of Water's Associates) columns. The series routinely used consisted of one 10³-nm, two 10²-nm, two 50-nm, and one 10-nm pore-size columns. THF at a flow rate of 1.0 ml/min was used as the eluant, with a 62-minute interval required for each injection to pass through the column (62 ml total elution volume).

The columns were standardized with 10 polystyrene standards (Water's Associates) ranging in molecular weight from 1 750 000 to 1200 daltons. In addition to the polystyrene standards, fatty acid esters with molecular weights near 450 and 300 daltons were also used to standardize the column set. A third-order fit for the standards gave a 99.87% correlation coefficient with an estimated error of 6%.

[GPC results obtained for extracts of tapes are reported as the amount of binder relative to lubricant and as the molecular weight (relative to styrene) for the peak maximum (M_p) of the molecular-weight distribution.]

• Results and discussion

The polyurethane elastomers used as binders for flexible magnetic tape are composed of segments or blocks of chemically different units. These elastomeric polyurethanes contain a flexible, low-melting-temperature portion (soft segment) connected to a more rigid, high-melting-temperature block (hard segment). Typically, the soft segment is composed of a repeating series of ester- or ether-linked units of relatively short chain lengths. The polyester soft-segment blocks are formed by the reaction of a difunctional carboxylic acid with a difunctional alcohol such that the resulting polymer is terminated primarily with alcohol end-groups. The polyether soft segments are

constructed through a number of pathways usually involving the ring-opening condensation of cyclic ethers to give alcohol-terminated, ether-linked polymers, also of relatively short chain lengths.

The effect of changes in the length of the soft segment is usually observed as an increase in the elasticity of the polyurethane made from the soft-segment polyol by the addition of difunctional isocyanate and a variety of chain extenders. The structure and chemical composition of the soft segment (i.e., polyester or polyether) play a significant role in achieving solubility and performance properties, as well as dictating the polyurethane's degradation resistance [10–12]. The soft-segment portion of a polyester- or polyether-polyurethane, therefore, plays a crucial role in defining the behavior of a given polyurethane binder for magnetic-tape applications.

The other block contained in these polyurethane binders is the hard-segment portion. These polymer blocks possess a markedly different chemical and mechanical behavior compared with that exhibited by the soft segments. The hard segments are usually constructed from diisocyanates, such as 4,4'-diphenylmethane diisocyanate (MDI), reacted with difunctional alcohols such as 1,4-butanediol. The resulting polymer consists of urethane-linked units of relatively short chain lengths (usually much shorter than the soft-segment polyol), which form rigid, high-melting-temperature (200°C) hard segments [13, 14]. The size and composition of the hard-segment blocks have been found to influence the hardness, modulus, and flow temperature of the polyurethane [10, 11, 14, 15]. For tape applications, a balance of properties is sought such that the binder is adaptable to the requirements of the recording device and pigmented coating.

The polyurethane hard segments associate through strong hydrogen bonds and dipole-dipole interactions. This results in the observed higher thermal stability of the hard segments and their association into domains within the polyester soft-segment phase. The separation of the hard segments into crystalline domains which are surrounded by an amorphous soft-segment phase gives rise to the observed thermomechanical properties associated with polyurethane elastomers [10].

The crystallinity of the soft-segment phase, as well as its miscibility with the hard segment, has been found to have a significant impact on thermomechanical properties. The effect of increased phase miscibility is an increase in the softening point of the polyurethane caused by the reduction in the interaction between the hard-segment blocks [16]. The importance of the phase separation and the disruption of phase morphology by the introduction of competitive interactions with magnetic metal oxides are important observations noted during the study of the chromium-dioxide-polyurethane coatings.

It was anticipated, from previously reported studies on the

effects of humid aging of magnetic tapes [17–20], that changes in the polyurethane would occur as a result of exposure to high temperature and humidity for extended periods of time. Hydrolysis of polyester-polyurethanes is well documented in the chemical literature [21–23] and is found to be the primary mechanism responsible for the deterioration of magnetic-tape performance after exposure to humid aging [17–19]. Hydrolysis involves the cleavage of the polyester chain of the soft segments by the addition of water to the ester linkages. This reaction produces alcohol and acid functional fragments, with a rapid reduction in the molecular weight of the parent polymer. The significance of such binder degradation to tape performance arises from the relationship between the molecular weight of the polyurethane and its ability to produce a cohesive film when filled with magnetic particles. In addition, as stated in the literature, low-molecular-weight products of hydrolytic degradation can migrate to the surface of the tape and produce contamination of the recording head, with resultant deleterious changes in signal quality and frictional properties [17, 18].

The motivation for the investigation of the impact of humid aging on tapes containing chromium dioxide is evident from the preceding discussion. Comparison of the susceptibility of the polyester- and polyether-polyurethanes to humid aging when they are used as binders for chromium dioxide was therefore undertaken to assess the archival performance of such tapes. A comparison with conventional formulations using $\gamma\text{-Fe}_2\text{O}_3$ as the magnetic pigment was thus carried out to establish a bridge to previous investigations [19, 20].

The results presented in **Figure 1** indicate that exposure to elevated temperature and humidity causes only slight or negligible changes in the molecular weight of the extractable binder for a tape containing $\gamma\text{-Fe}_2\text{O}_3$ as the magnetic pigment. These slight changes may be evidence of hydrolytic degradation of the binder or simply the result of adsorptive fractionation of the lower-molecular-weight portion of the original binder molecular-weight distribution. The lubricant peak in the GPC chromatogram, when used as an internal standard, suggests that the latter explanation is probably operative for the $\gamma\text{-Fe}_2\text{O}_3$ -pigmented tape. The small increase in extractable binder with a slightly higher molecular weight indicates increased binder extraction after humid aging. This result is not evidence of hydrolytic degradation. In addition to the apparent failure to detect appreciable hydrolytic degradation by GPC analysis of the $\gamma\text{-Fe}_2\text{O}_3$ -tape extract, no change in the infrared spectrum of the extracted material could be detected. For these iron-oxide tapes, little evidence for appreciable hydrolytic degradation was noted for tapes exposed to 52°C/30–60% RH for periods of several months.

When chromium dioxide is substituted into the same coating formula as was used to construct the $\gamma\text{-Fe}_2\text{O}_3$ tape

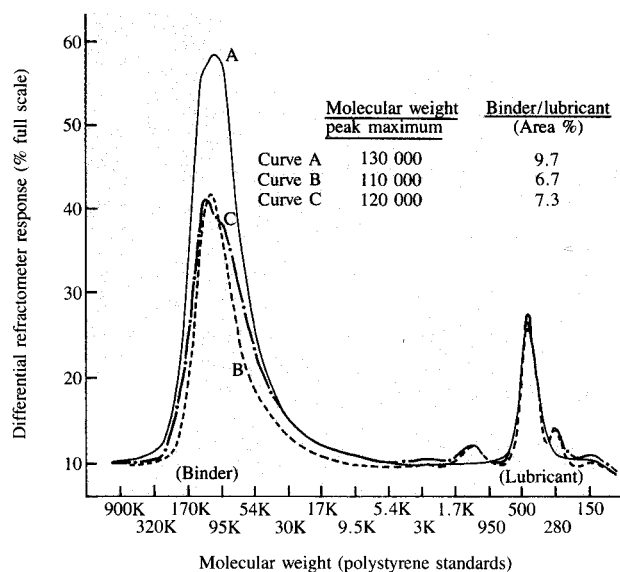


Figure 1

Gel-permeation-chromatographic separation of $\gamma\text{-Fe}_2\text{O}_3$ with resin A. Curve A: THF solution of resin A with lubricant, without $\gamma\text{-Fe}_2\text{O}_3$; Curve B: THF extract of tape before humid aging; Curve C: THF extract of tape after humid aging for 21 days at 52°C/30% RH.

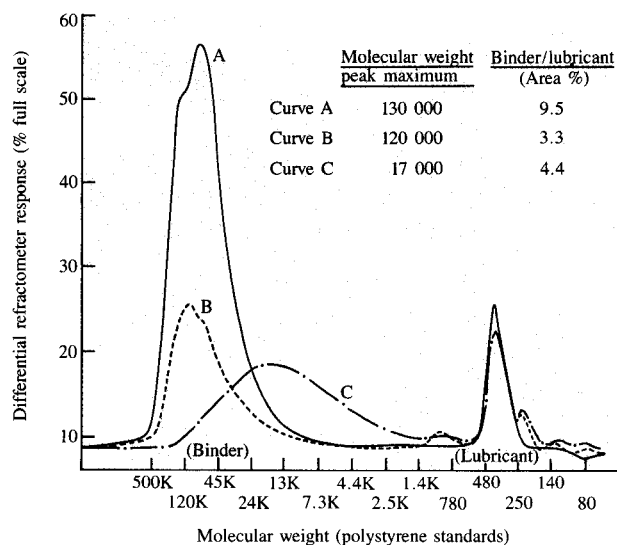


Figure 2

Gel-permeation-chromatographic separation of chromium dioxide with resin A. Curve A: THF solution of resin A with lubricant, without chromium dioxide; Curve B: THF extract of tape before humid aging; Curve C: THF extract of tape after humid aging for 21 days at 52°C/30% RH.

(Fig. 1) with resin A, a significant change in the extractable binder is observed (Figure 2). Comparison of the GPC chromatograms taken for both tape extracts indicates two striking differences. The first difference is that considerably more binder is initially insolubilized on the chromium dioxide despite similar curative conditions and loadings. This result is evidence of the significant difference in the wetting interaction of the two pigments with the same polyester-polyurethane.

The other difference observed in the results is the significant reduction in the molecular weight of the extracted binder after exposure to aging at 52°C/30% RH for 21 days. The decrease in molecular weight from 120 000 to 17 000 daltons is dramatic. In contrast to the results obtained for the $\gamma\text{-Fe}_2\text{O}_3$ -pigmented tape, the amount of extractable, low-molecular-weight material cannot be attributed to fractionation of the initial polyurethane. The ratio of extractable binder present in the chromium-dioxide-resin A tape relative to the lubricant as measured with the GPC (by peak area ratio) was found to be less than 3.3 initially and increased to 4.4 after exposure to humid aging. The apparent decrease in the molecular weight of the extractable binder, accompanied by an increased amount of extractable binder, is believed to be strong evidence for hydrolytic degradation of the polyester segments rather than nondegradative fractionation of the binder, as is believed to be the case for the iron-oxide tape.

Freshly prepared chromium-oxide-resin A tape subjected to 52°C/30% RH for 10–14 days was found to give the same level of degradation as that obtained after one year of ambient storage. In addition, the low-molecular-weight fragments were found to migrate to the tape surface, leading to a substantial change in the frictional properties of the tape.

The unaged chromium-dioxide tape performed satisfactorily on a conventional digital-recording tape drive. The same tape, after exposure to 42°C/20% RH for 29 days, still performed at an acceptable level, but an audible noise was detected by the operator during tape motion, indicating some change in the ease of the unwinding of the tape from the reel. Another reel of the same tape, after exposure to 52°C/30% RH for 48 days, not only produced the audible noise during tape motion, but upon stop-start operations produced adhesion of the tape to the recording head and failure of the drive to move the tape on command. Additional aging at 52°C/30% RH for 82 days produced a severely degraded tape which could not be moved through the tape path nor readily unwound from the reel.

Examination of the recording head after running such degraded tape over the surface showed considerable tacky contamination, which was identified by mass spectrometry as consisting primarily of polyester fragments. Considerably fewer of the mass spectral ions associated with the polyurethane hard segments were observed in the mass

spectra of the head contamination resulting from these degraded tape tests than were found present in either the undegraded binder or the extracts of the degraded tape. Presumably, the polyurethane fragments produced by hydrolytic degradation of the soft segments, although present in the THF extracts of the tape, do not migrate to the tape surface as readily as the low-molecular-weight, polyester-rich degradation fragments.

To stabilize the recording performance of chromium-dioxide tapes, the mechanism of degradation, apparently catalyzed by the chromium dioxide, was investigated. Degradation of resin A when combined with chromium dioxide was found to be accelerated with higher-temperature storage at a given humidity and at higher humidity for a given temperature. These observations are represented graphically in Figures 3 and 4. No change in the molecular weight of the extracted binder, attributable to hydrolytic degradation, was noted for the tape stored under dry conditions. The decrease in the amount of extractable binder (Fig. 4) observed for the tape stored at 52°C in a desiccator could be convincingly accounted for as simple fractionation of the polymer, with the lower-molecular-weight fraction requiring the longest thermal aging to become insolubilized in the coating.

Because no apparent degradation could be detected for tapes aged under dry conditions, we concluded that water is required to obtain the scission of the polyester linkages. Such hydrolytic degradation of polyester-polyurethanes is well documented in the chemical literature [21-23].

From a survey of the relevant literature, potential improvements in the resistance of the polyester-polyurethane to hydrolytic degradation could be anticipated from the incorporation of a carbodiimide stabilizer [21, 23], the use of polyethers [23, 24], or the selection of more hydrolytically stable polyesters [21, 24]. All of these potential remedies were investigated.

Because acid-catalyzed hydrolysis of the polyester has been shown to increase the rate of polyester-polyurethane degradation [21, 23], the use of acid-scavengers such as polymeric carbodiimides has been found to be a useful method of stabilization [21, 23]. When 2% (relative to the weight of polyester-polyurethane) of a polymeric carbodiimide was added to a resin A-chromium dioxide formulation, however, no appreciable inhibition of the polyester-polyurethane degradation was noted (Figure 5). This result appears to contradict the experience reported in the literature [21, 23]. It is relevant to note, however, that the prior work involving the use of such stabilizers studied unfilled free films and that the present study is attempting to characterize a highly filled system. In fact, the majority of the free films studied in this work are loaded very near to the critical pigment-volume concentration (CPVC) with a hard, reactive, acicular particle. It therefore is reasonable to interpret the inability of the carbodiimide to stabilize

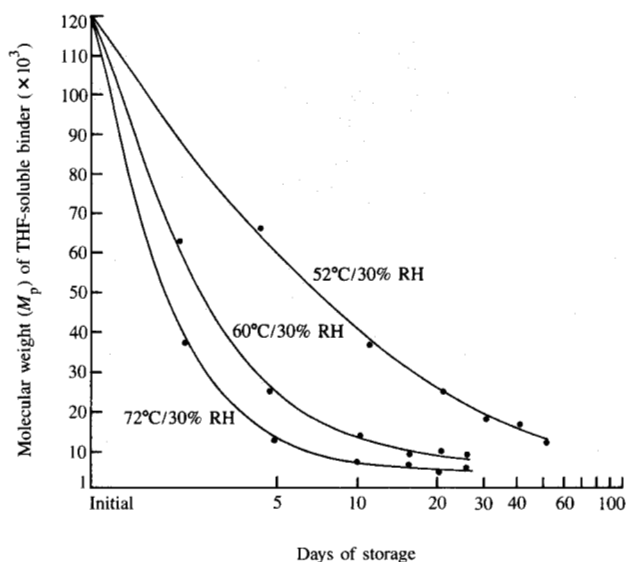


Figure 3

Change in the molecular weight of the extractable binder for the chromium-dioxide-resin A tape; effect of storage under different environmental conditions.

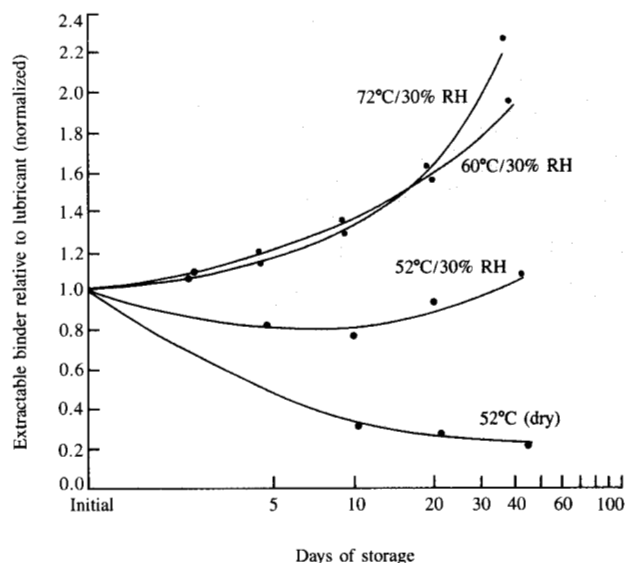


Figure 4

Change in the amount of extractable binder relative to the lubricant for the chromium-dioxide-resin A tape; effect of storage under different environmental conditions.

polyester-polyurethane binder hydrolysis in such a filled system as being further evidence of the strength of the

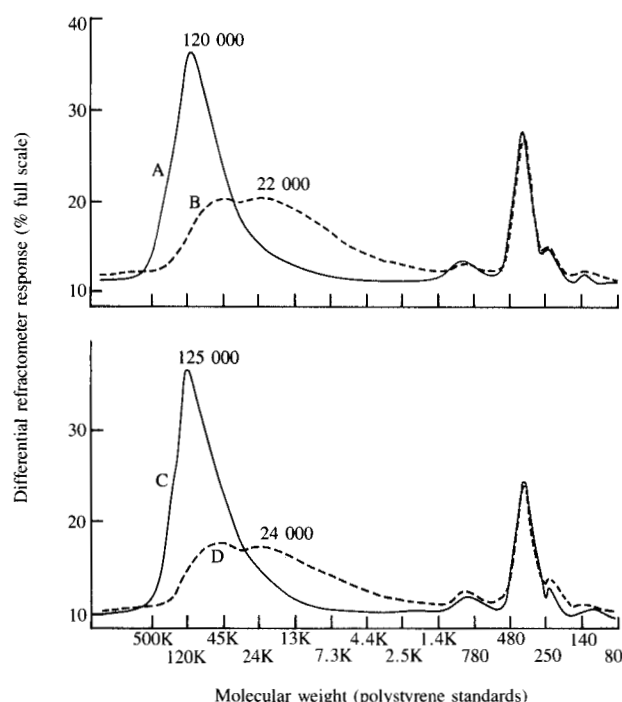


Figure 5

Gel-permeation-chromatographic separation of chromium-dioxide-resin A tape containing carbodiimide stabilizer. Curve A: THF extract of unstabilized tape before humid aging; Curve B: THF extract of unstabilized tape after 21 days at 52°C/30% RH; Curve C: THF extract of stabilized tape before humid aging; Curve D: THF extract of stabilized tape after 21 days at 52°C/30% RH.

interactions of the urethane polar groups with the chromium-dioxide surface. This conceptualization leads to the suspicion that the tenacious adsorption of the polyurethane to the chromium-dioxide surface might preclude the effectiveness of a stabilizing additive in mitigating the chromium-dioxide-catalyzed degradation of the polyester portions of the binder.

The substitution of a thermoplastic polyether-polyurethane was expected to offer a more fruitful resolution to the binder degradation associated with formulations based on chromium dioxide because their resistance to hydrolysis is well documented [21, 24]. When a polyether-polyurethane (resin C) was substituted into the chromium-dioxide formulation, however, quite the reverse was observed (Figure 6). The amount of extractable binder of such low molecular weight prior to humid aging was unexpected. Examination of the GPC results obtained for the polyether-polyurethane before milling with the chromium dioxide indicated a narrow molecular-weight distribution with a peak maximum at 120000 daltons. The extract obtained from the chromium-dioxide-resin C tape before aging gives an

extremely broad distribution, with its peak maximum near 8200 daltons. The amount of extractable material, furthermore, was extremely large and actually exceeded the initial ratio of the binder relative to the lubricant, as measured by the differential-refractometer detector. This presumably results from a significant change in the refractive index of the fragments relative to the initial polymer.

The results obtained for the extract of the aged tape (Fig. 6) indicate that the humid aging increased the degradation of the polyether-polyurethane, but the significant observation to be derived is the apparent sensitivity of the polyether-polyurethane to the addition of chromium dioxide. Because the degradation is observed to occur without the environmental exposure, hydrolytic degradation does not appear to offer a reasonable explanation of the observed changes in the polyether-polyurethane in the presence of chromium dioxide. Oxidative chain scission of the polyether portion of the polymer occurs for these polyurethanes, giving rise to low-molecular-weight products and rapid deterioration of tape performance.

From the preceding discussion, it appears that stabilizers and polyether-polyurethanes might not offer a suitable solution to the apparent binder degradation induced by chromium dioxide. As a result, a hydrolytically stable polyester-polyurethane was sought as a potential solution to the binder degradation.

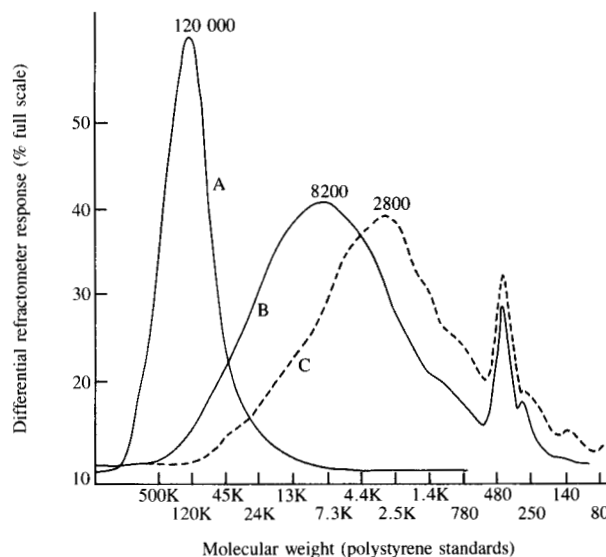


Figure 6

Gel-permeation-chromatographic separation of chromium-dioxide-resin C tape. Curve A: polyether molecular weight distribution before addition to chromium dioxide; Curve B: THF extract of tape before humid aging; Curve C: THF extract of tape after 21 days at 52°C/30% RH.

The exceptional hydrolytic stability of a polyester-polyurethane containing sterically hindered alcohols in the polyester of the soft-segment phase was noted in the early work of Schollenberger [21]. As a result, a chromium-dioxide formulation using a polyester-polyurethane composed of such a hindered alcohol ester as the soft segment was investigated (resin B).

GPC analyses of the THF extracts obtained for the chromium-dioxide-resin B tape after exposure to humid aging, presented in **Figure 7**, indicate the relatively slow rate of hydrolytic degradation exhibited by this polyester-polyurethane.

The GPC results shown in Fig. 7 indicate a surprising effect, which was noted for the chromium-dioxide-resin B tape extracts. Initially, humid aging at 52°C produces extractable binder that can be readily ascribed to fractionation of the initial molecular-weight distribution of the polymer rather than to hydrolytic degradation. Continued exposure to humid aging past the first few weeks at this environment then begins to liberate increased amounts of low-molecular-weight material. This is presumed to indicate the presence of competitive processes that are operative during the thermal and humid aging of the coating.

The initial drop in the molecular weight of the THF-extracted binder is readily accounted for by insolubilization of the polyester-polyurethane on the surface of the chromium-dioxide particle. Indeed, as indicated by the DMA data for such environmentally aged tape, which is discussed below (see also Fig. 14, shown later), the increased insolubilization of the polymeric binder on the particle is indicated by an increase in modulus during the first few weeks of aging. This would be expected for a reinforced material where thermally induced interactions leading to increased adsorption of the binder on the filler particles take place [25, 26]. It is reasonable, therefore, to ascribe the initial decrease in the molecular weight of the extractable binder to the fractionation of the polyester-polyurethane rather than to hydrolytic degradation.

Continued exposure to humid aging is then observed to give an increased amount of extractable binder with a decrease in molecular weight, as indicated in the GPC results presented in Fig. 7, Curve D. This result is believed to be a consequence of the competition between water vapor and the urethane polar groups for the adsorption sites on the surface of the chromium-dioxide particle. As the water successfully infiltrates the urethane-particle interface, disruption of previously insolubilized binder occurs, resulting in the marked increase in the extractable material. That this explanation is appropriate is further demonstrated by the results obtained after exposure to dry thermal aging (Figure 8).

The results presented in Fig. 8 were obtained by placing a chromium-dioxide-resin B tape into a desiccator at 52°C for

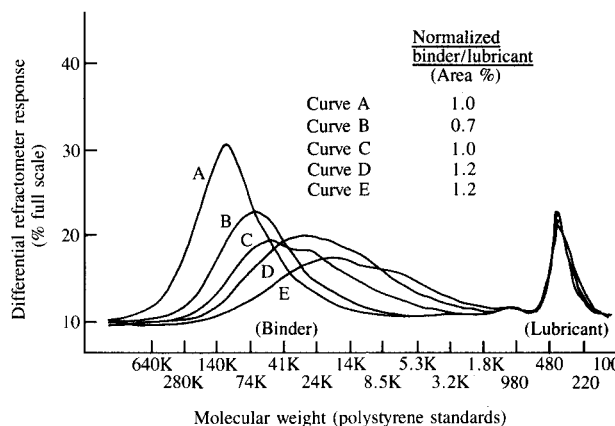


Figure 7

Gel-permeation-chromatographic separation of chromium-dioxide-resin B tape extracts: Curve A: THF extract of tape before thermal aging; Curve B: THF extract after three days at 52°C/60% RH; Curve C: 21 days at 52°C/60% RH; Curve D: 36 days at 52°C/60% RH; and Curve E: 60 days at 52°C/60% RH.

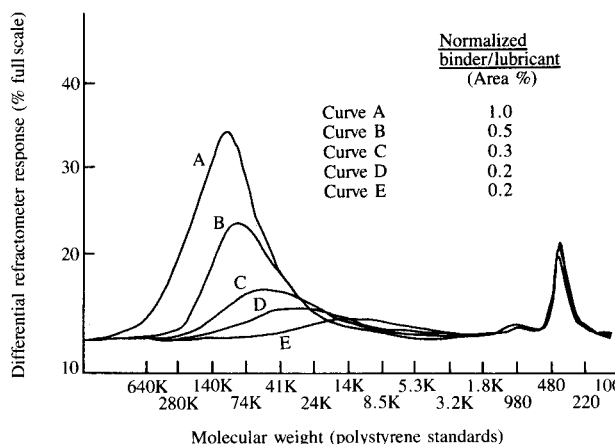


Figure 8

Gel-permeation-chromatographic separation of chromium-dioxide-resin B tape extracts. Curve A: THF extract of tape before thermal aging; Curve B: THF extract after three days at 52°C; Curve C: 21 days at 52°C (dry); Curve D: 36 days at 52°C (dry); and Curve E: 60 days at 52°C (dry).

periods up to 60 days. The THF extracts of this sample produced the series of GPC chromatograms shown. The extract concentrations were adjusted to an equivalent amount and gave reproducible peak heights for the lubricant peak, thus permitting the superposition of the series of traces to give what is readily seen as a continuous fractionation. As dry thermal exposure is continued, the urethane insolubilization increases, with the lower-molecular-weight

fraction remaining soluble for the longest period. This presumably arises from the fact that more adsorption sites are present for the higher-molecular-weight polymer chains, which must subsequently be disrupted by the extraction solvent to effect solubilization. The shorter chains, having fewer polar sites capable of being tightly held on the particle surface, remain relatively soluble.

Comparison of the results obtained after humid thermal aging with those obtained for a similar tape exposed to dry thermal aging (Figs. 7 and 8) indicates that for the chromium-dioxide-resin B formulation the primary action during the initial aging period is the insolubilization of the binder and an increase in the cohesive integrity of the coating, as shown by its dynamic mechanical analysis (DMA) response (Fig. 14). These results, as well as those obtained at various temperatures and humidities, demonstrated that the improved hydrolytic stability gained by the inclusion of the hindered alcohol-ester into the soft segment of the polyester-polyurethane dramatically improved the chemical and mechanical stabilities of the chromium-dioxide formulation.

The impact of humidity on the performance of the coating, furthermore, was found to be significantly reduced, although not eliminated. We noted, moreover, that even upon severe degradation of resin B after exposure to 72°C/60% RH for 140 days, some of the apparent reduction in the molecular weight of the extractable material could be ascribed to fractionation of the molecular-weight distribution of the original polyester-polyurethane, rather than to hydrolytic degradation of the polyester. This is not to say that the extractable degradation products did not display evidence of oxidation or hydrolysis, only that the extent to which hydrolysis had an impact on the binder integrity had been dramatically reduced, such that no impact on functional performance was detectable in the final tape, even under extreme use conditions.

It appears that a resolution to the binder degradation imposed on magnetic-tape coatings containing chromium dioxide has been successfully obtained. The hydrolytic stability of the polymeric binder has been significantly improved by the use of a hydrolytically stable polyester-polyurethane.

Mechanical stability

As mentioned previously, when higher recording densities are achieved, the mechanical properties of the tape surface become increasingly important. The stability of both the recording performance and the frictional properties depends to a large extent on the stability of the mechanical characteristics of the tape surface. The exceptionally smooth finishes required on the tape and the recording-head surfaces can lead to undesirably high friction values. Changes in the characteristics of the tape surface also lead to changes in the recording characteristics, particularly to changes in

amplitude, and to changes in frictional performance. The frictional forces can become catastrophically high if the tape surface takes on the extreme smoothness of the base film under the interlayer pressures encountered when the tape is wound on a reel.

The frictional force in elastomeric systems consists of contributions from adhesion forces and hysteresis forces. The hysteresis term in viscoelastic (rubbery) materials is caused by a delayed recovery of the elastomer after indentation by an asperity. The adhesion term is a result of the shearing of adhesive bonds formed at the interface in the region of the real area of contact. For magnetic-tape applications using polyurethane binders and operating under normal conditions, the adhesion component of friction is the most significant; the hysteresis component is negligible [27].

The adhesion component of friction (f_A) is defined as the product of the real area of contact (A_r) and the shear strength of adhesion (τ_a) between the contacting surfaces,

$$f_A = A_r \tau_a \quad (1)$$

The real area of contact for elastic contacts (true for light loads) is given by

$$A_r \sim 3.2W/E_c \sqrt{\sigma_p/\beta_p} \quad (2)$$

and for plastic contacts,

$$A_r \sim W/H, \quad (3)$$

where W is the normal load, E_c is the reduced complex modulus, H is the indentation hardness, and σ_p and β_p are the composite standard deviation and mean radius of curvature of the upper 25% of the asperity contacts, respectively [27].

For most tape contacts in magnetic-tape drives, the asperity contacts are elastic. For elastic contacts, the real area of contact depends on the complex modulus and surface topography; the coefficient of friction depends on the shear strength at the interface of contacting asperities. The mechanical-property values used in these friction calculations must be obtained at appropriate rates of deformation and shear-strain [27].

The response of a given tape to applied stresses is determined by these and other mechanical properties of the magnetic coating and the substrate beneath it. Given sufficient time, a compressive stress can lead to a dramatic increase in the real area of contact and a resultant increase in friction [28]. The mechanical properties of the binder system may also be altered by exposure of the tape to high temperature, humidity, or both [29].

When the creep-deformation rate is unduly high, large areas of real contact can be developed in relatively short periods of time, resulting in high frictional forces. Creep-deformation rates may be influenced by pressure, temperature, and relative humidity. The interlayer pressure in a wound reel is highest near the hub. Therefore, it can be

expected that any changes in the surface characteristics will be greatest near the hub, particularly if the coated surface is pressed against an extremely smooth substrate surface.

• *Experimental results and discussions*

The interlayer radial pressures in the 3480 data cartridge were measured by inserting shims between the layers of tape during winding at a wind tension of 2.2 N. The shims were removed using an Instron force-measuring device. The pull force required to remove the shim was then calibrated to the interlayer pressures using multiple layers of tape between blocks with known clamping forces. The results are shown in **Figure 9**. Near the hub, interlayer pressures were measured to be approximately 1.7 MPa.

A number of tapes made by various tape manufacturers were wound on the 3480 reels. Stress conditions for measuring changes related to creep deformation were selected to be 52°C and 60% relative humidity. Tapes were wound on the reels at 2.2 N of tension. Frictional measurements were then taken at selected intervals in the reel from the beginning of tape (BOT) to the end of tape (EOT) near the hub. Initially, measurements were made before the wound reels were subjected to the elevated temperature and humidity conditions, and then they were repeated after two-day stress periods. The measurements were made at 32°C and 87% RH. Tapes were conditioned to the test environment for 24 hours before being measured. Measurements were made on a model of the 3480 tape path. Because creep deformation caused by interlayer pressures is greatest at EOT, only EOT frictional measurements are

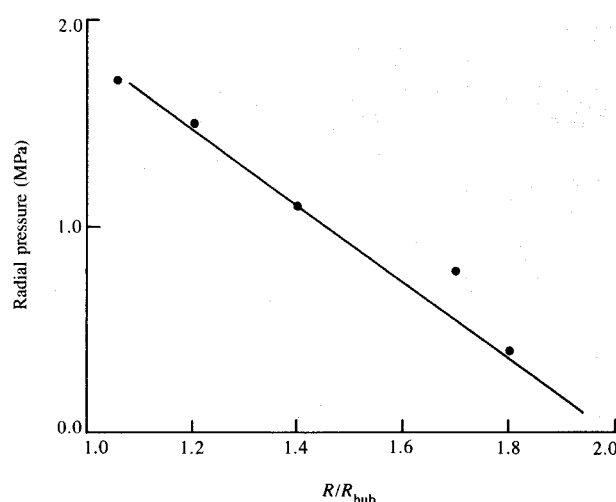


Figure 9

Interlayer radial pressures as a function of normalized radial position in the reel, R/R_{hub} , at a wind tension of 2.2 N.

reported. The frictional measurements consisted of locating the end of tape at the head, relieving tension, and manually pulling the tape under initial tension of about 0.5 N provided by the drive motor. The breakaway force required to pull the tape was measured by a tensiometer. The wrap angle of the head was about 15°. The results are shown in **Table 1**. The effect of creep deformation caused by increasing interlayer pressures (decreasing radial reel

Table 1 Static friction at end of tape for different tapes (stressed at 52°C and 60% RH, in time); tension (T_0) = 0.5 N, wrap angle = 15°.

Tape no.	Friction (Δ tension) with stress time (g)						
	0 days	2 days	4 days	6 days	8 days	18 days	22 days
1	0.55	0.55	0.55	0.55	0.55	0.55	0.55
2	0.55	>3.4	—	—	—	—	—
3	0.55	>3.4	—	—	—	—	—
4	0.55	>3.4	—	—	—	—	—
5	0.60	0.65	0.60	0.60	0.60	0.65	0.60
6	0.50	0.95	1.9	2.5	>3.4	—	—
7	0.55	>3.4	—	—	—	—	—
8	0.55	0.85	1.0	1.4	1.9	2.2	2.7
9	0.50	0.50	0.55	0.50	0.50	0.55	0.50
10	0.50	0.55	0.50	0.50	0.55	0.50	0.55
11	0.50	0.50	0.50	0.55	0.50	0.50	0.50
12	0.55	>3.4	—	—	—	—	—
13	0.60	0.65	1.2	1.3	1.6	1.7	1.8
14	0.55	1.6	2.2	>3.4	—	—	—
15	0.50	0.55	0.50	0.55	0.55	0.50	0.50
16	0.45	0.60	0.95	1.1	1.2	1.7	2.0
17	0.45	0.45	0.40	0.45	0.45	0.50	0.50
18	0.50	0.45	0.50	0.50	0.55	0.50	0.50
19	0.55	0.95	1.0	1.2	1.3	1.4	1.6
20	0.60	1.2	1.6	1.9	2.2	>3.4	—

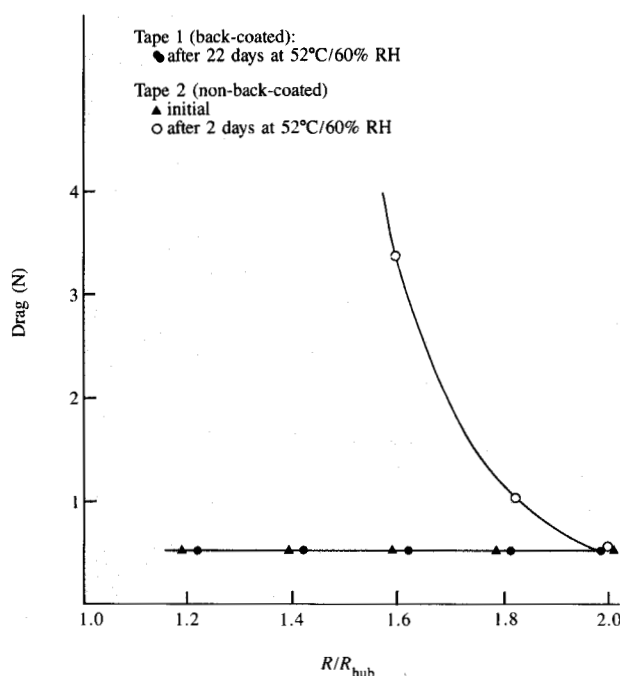


Figure 10

Effect of increasing friction as a function of normalized radial position in the reel.

position) for tape 2 after two days at 52°C and 60% RH is shown in Figure 10.

Of the original tapes used in the experiment, the ones that showed the most stable frictional properties were 1, 5, 9, 10, 11, 15, 17, and 18. All of these eight tapes were back-coated, except for tapes 15 and 17. The binder systems of these two tapes contained a hard, organic polymer additive in significant ratios to the base polyurethane binder.

These results led to another experiment, in which identical coatings were applied to substrates of increasing smoothness. The same high-temperature and relative-humidity conditions and measurement intervals were used. Four substrates with varying smoothnesses were selected. By varying the surface smoothness, the friction could be varied from 0.5 to above 5 N. The experiments showed the important role that the surface finish of the substrate plays in influencing the forces developed by creep deformation.

Creep deformation of the tape surface under pressure, accelerated by elevated temperature and humidity, appeared to be the operative rationalization for the changes in frictional properties resulting from storage under these conditions. Final confirmation of this mechanism for increased real areas of contact was shown by an experiment in which tapes with identical coatings were subjected to environmental stressing at 52°C and 60% RH. One of the tapes was back-coated and the other two were not. The back-

coated tape and one of the tapes without a back coat were wound on a 3480 cartridge reel under 2.2 N of tension. The remaining tape that was not back-coated was subjected to the same environment but under zero interlayer pressure conditions. Normal tension was reestablished before measurement, and the results are shown in Figure 11. Of the two tapes wound at 2.2 N of tension, the tape without back-coating showed high frictional results after this environmental exposure, whereas the back-coated tape maintained its low frictional properties. The tape wound at zero tension maintained its low frictional properties.

Dynamic mechanical analysis (DMA) was performed on free films of the chromium-dioxide-polyester-polyurethane formulations using a du Pont DMA Model 981 with heating rate of 10°C per minute. The details of the DMA investigation are reported elsewhere [27, 28]. In general, the motivation for the DMA study of the chromium-dioxide formulations was rooted in the observation that the frictional properties of various tape formulations appeared to be highly dependent on their previous thermal and stress histories. As shown in Figure 12, the frictional properties of various tapes subjected to aging at 52°C under compressive stresses were found to depend significantly on the complex modulus, as measured by DMA at the stress temperature. Despite various other factors, such as changes in binder composition, loading, cure conditions, initial surface roughness, and method of dispersion, stable frictional behavior was exhibited only by those tapes that displayed a complex modulus greater than 1.2–1.5 GPa at 52°C.

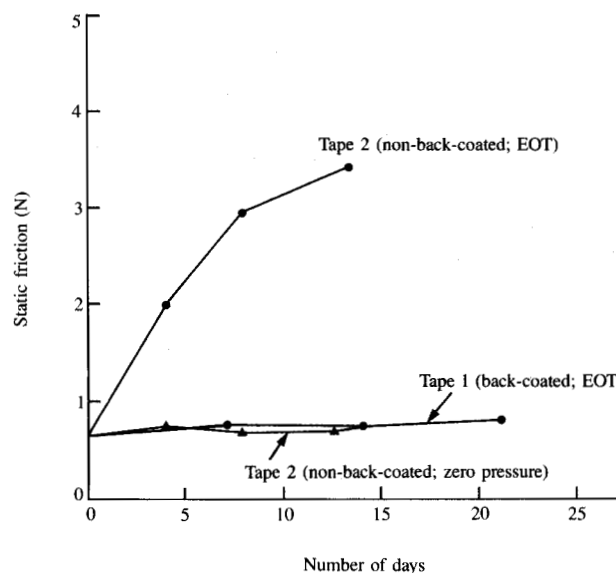


Figure 11

Static friction as a function of aging at 52°C/60% RH.

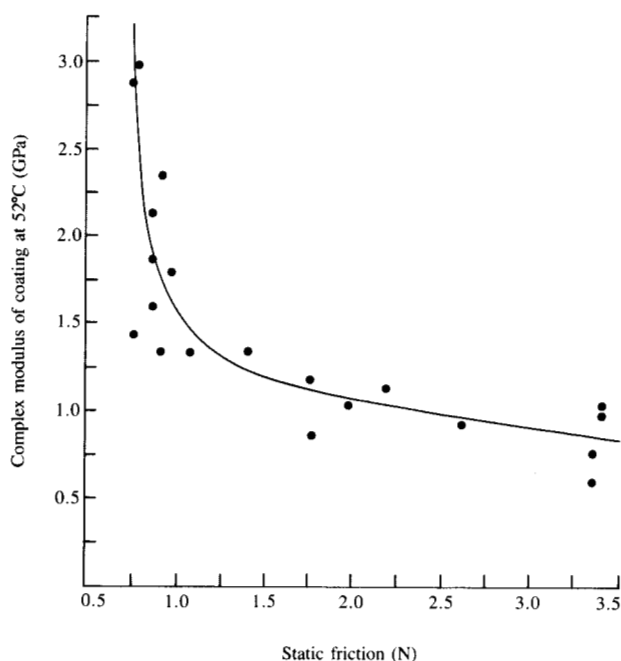


Figure 12

Frictional properties of tapes having different chromium-dioxide formulations (the data points) after aging at 52°C; depicted in terms of associated values of complex modulus and static friction.

Measurement of the dependence of the coefficient of friction on temperature, furthermore, revealed a noticeable inflection temperature which corresponded reasonably with the temperature observed in the modulus curves obtained by DMA (Figure 13). These observations suggested that at a temperature dictated by the thermomechanical properties of the coatings, the real area of contact between the tape asperities and the mating tape-drive surfaces can undergo a rapid increase under an applied stress. The stresses to which the asperities are exposed presumably determine the critical modulus at which compression of the asperities begins to become appreciable. After the critical temperature (modulus) is exceeded, the coefficient of friction is found to increase dramatically (Fig. 13).

As we noted earlier, the polyester-polyurethane binders have been found to exhibit considerable interaction with the chromium-dioxide particles. Aside from the degradative effects already discussed, the polyurethane binders have been found to display a marked sensitivity to their thermal and environmental histories [29]. As shown in Figure 14, when a free film of chromium-dioxide formulation is exposed to humid thermal aging, the modulus is found to increase significantly. This appears to be the result of thermally induced phase separation permitting greater wetting interactions with the chromium-dioxide particle. Such effects from thermal aging are not unusual for filled coatings,

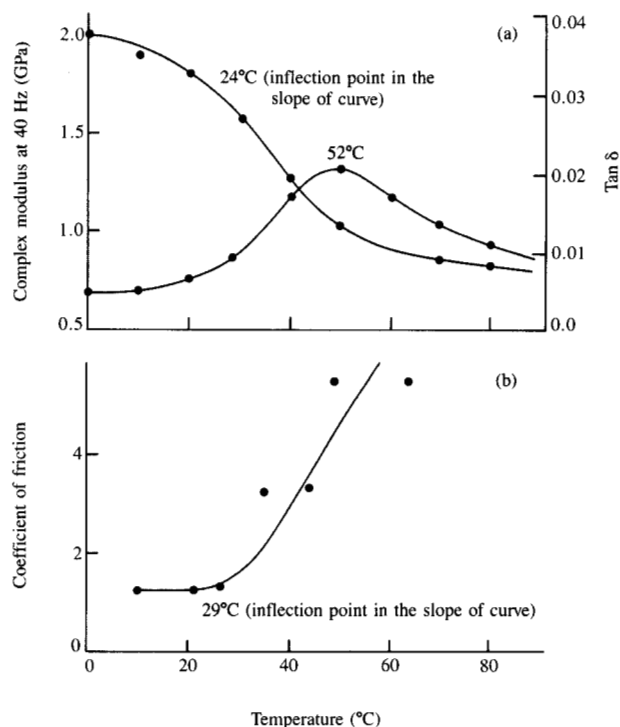


Figure 13

Temperature dependence of the complex modulus of chromium-dioxide-resin B tape (a) and of its coefficient of friction (b).

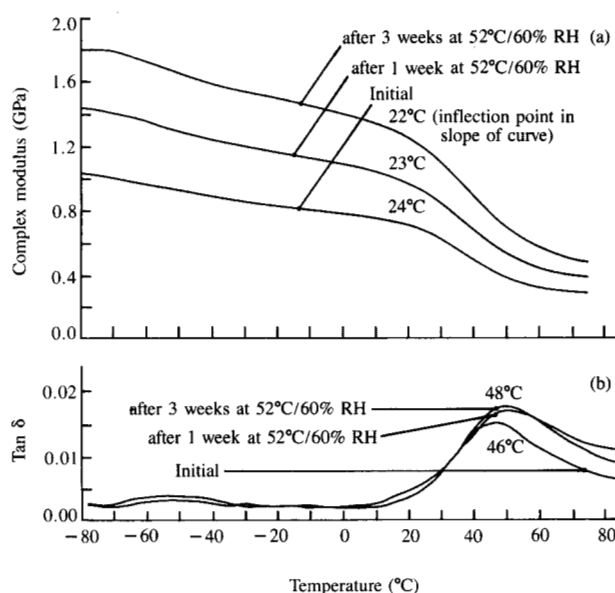


Figure 14

Dynamic mechanical analysis of chromium-dioxide-resin B free films; effect of humid and thermal aging on bulk mechanical properties: (a) complex modulus vs. temperature; (b) $\tan \delta$ vs. temperature.

Table 2 Static friction at end of tape for various head modifications using the same tape (with high frictional properties). Tension ~ 0.5 N; wrap angle = 15° .

Head modification	Surface roughness (center line average) (μm)	Friction (Δ tension) at EOT (N)
Standard	0.005	2.0
Flame-sprayed	0.15	1.6
Chrome-plated	0.52	1.3
Sand-blasted	0.660	1.1

especially for those involving strong polar-bond interactions [25, 26].

The increase in the modulus of the coating after thermal aging suggests that a tape subjected to such aging without smoothening compressive forces should exhibit increased stability in its frictional performance as a result of the increased modulus. This was found to be the case for the experiment discussed before, in which a set of tapes was exposed to humid thermal aging. One of the tapes was subjected to compressive stresses and was found to exhibit a marked increase in frictional properties, especially near the reel hub, where the compressive forces are greatest. Another tape, which had been stored without any applied compressive force, was found to exhibit normal frictional behavior. When this thermally aged, low-friction tape was returned to the humid aging environment, with the compressive forces renewed, the effect of the increased modulus during the first environmental cycle was marked. Only a slight change in the frictional properties near the hub was measured. This result provided convincing evidence of the importance of the modulus of the coating in maintaining the frictional performance of the tape.

Methods for modifying the frictional forces at the head-to-tape interface were also investigated. One method was to reduce the contact area of the head. This approach is somewhat counterproductive, because a reduction in the apparent contact area results in a proportional increase in the pressures generated at the now lessened areas of real contact. Also, higher recording densities dictate that the head-to-tape separation be minimal. Table 2 shows the results of many head-modification experiments.

Another method for modifying the frictional forces at the head-to-tape interface is through careful control of the surface topography of the tape. As seen from previous discussions and experimental results, this method can be frustrated by the time-dependent creep-deformation characteristics of the tape surface.

The most effective surface-topography control techniques for magnetic tape appear to be the addition of a rougher (0.063 – 0.075 μm rms) back coat or the use of a binder system with a large complex modulus. Although back-coated tape is commonly used for magnetic tape, its use to control

surface topography is not usually claimed. Generally, back-coating is claimed to control migration of contaminants out of the substrate [30] and static buildup in the tape path [31]. The experimental data (Table 1, tapes 1, 5, 8, 10, 11, and 18) show the effectiveness of the back coat in controlling surface-topography changes under the pressures encountered in a wound reel. The back coating reduces the high localized pressures encountered at the asperity contact points. Deformation caused by creep is controlled by the surface characteristics of the back coat, which, in turn, maintains the frictional characteristics of the recording surface.

Control of the complex modulus is somewhat more difficult but can be accomplished by careful design of the binder system. Both the inclusion of hard, glassy polymers and the tailoring of a single polymer are effective in controlling the creep-deformation rate. The binder system and resultant modulus must be designed around the "use" temperature of the tape product. This ensures the stability of the tape surface and thus maintains its frictional characteristics without substantial risk of disturbing other performance requirements, such as abrasion resistance and head wear.

Conclusions

The magnetic particles of chromium dioxide possess inherently attractive properties for use in digital magnetic recording. The implementation of conventional polyurethane-binder technology with chromium-dioxide formulations, however, necessitated more consideration of the particle-binder interactions than was necessary for other magnetic-particle systems. The chemical and mechanical stabilities of the finished coating were found to require specific chemical properties in the binder for formulations based on chromium dioxide.

Oxidative reactions at the binder–chromium-dioxide interface affecting the functionality of the polyurethane hard segments were not found to produce a deleterious effect on tape performance. Hydrolytic degradation of the polyester soft segments, however, was found to be accelerated by the interaction with the chromium-dioxide particles and had an impact on the mechanical performance of the tape upon exposure to humid aging. A hydrolytically stable polyester-polyurethane was found to offer a significant improvement in the resistance of the coating to binder degradation.

Careful control of the mechanical properties and maintenance of a stable surface topography were found to be necessary for acceptable tape performance. The deformation of the coating under compressive stresses was found to require consideration of the modulus of the coating at the applied stress conditions and of the control of the surface topography and frictional properties of the coating.

Additional improvements are to be anticipated as a result of continuing studies of the complex interactions involved in

magnetic-coating formulation for flexible magnetic tape. Current knowledge has permitted the manufacture of a tape containing chromium dioxide that has significantly improved chemical and mechanical performance, even under extreme environmental conditions. The insights obtained from this effort promise to provide the technology necessary to satisfy the demands of the digital-recording industry for particulate media using chromium dioxide well into the future.

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